APCAT B4

Performance of silica-supported copper oxide sorbents for SO_x/NO_x -removal from flue gas

II. Selective catalytic reduction of nitric oxide by ammonia

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Abstract

The selective catalytic reduction (SCR) of nitric oxide by ammonia was studied for silica-supported copper oxide particles to be used as a sorbent/catalyst in a continuous process for the simultaneous removal of SO_x and NO_x from flue gases. The SCR-behaviour was determined as a function of the sulphation degree, i.e. the fraction of copper oxide converted to copper sulphate, at temperatures ranging from 20 to 450°C. Up to 350°C, the fresh catalyst with 0% CuSO_4 showed a high selectivity towards production of nitrogen and water by the reaction of nitric oxide with ammonia and oxygen. At higher temperature, nitric oxide removal efficiencies decreased due to the oxidation of ammonia by oxygen. With an increase of the sulphation degree, the maximum temperature for selective catalytic reduction of nitric oxide gradually increased up to 420°C for a sulphation degree of 80%. In addition, the maximum nitric oxide removal efficiency increased as well. After regeneration of catalyst particles with a sulphation degree of 80%, realised by reduction with hydrogen and subsequent re-oxidation, the catalytic behaviour was similar to that of fresh catalyst particles with a sulphation degree of 5%. This is ascribed to the formation of some Cu_2S during the reduction, which is oxidised to CuSO_4 in the subsequent oxidation step. Since the selectivity towards the reduction of nitric oxide with ammonia is maintained up to about 375°C, a temperature which is very suitable for SO_x removal as well, the silica-supported CuO investigated can be applied as a sorbent/catalyst for the simultaneous removal of SO_x and NO_x from flue gases. The reaction rate constants for SO_x and NO_x removal appeared to be of the same order of magnitude provided that the reduced sorbent/catalyst enters the absorber directly, i.e. without a separate pre-oxidation.

Keywords ammonia, combined SO_x/NO_x removal, copper oxide, copper sulphate, kinetics, selective catalytic reduction, copper oxide/silica

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INTRODUCTION

Over the past 20 years several reports have appeared on the use of copper oxide (CuO) for the removal of SO_x [1-3] or, in combination with ammonia (NH_3) injection, for the simultaneous removal of SO_x and NO_x from flue gases [4-6]. The processes presented are regenerative and dry, and avoid stack gas reheat and a large water consumption.

Generally, CuO is deposited on a porous support to create an active sorbent/catalyst with a high stability. SO_x reacts in the absorber of these processes with the supported CuO and oxygen to copper sulphate (CuSO_4) at 300–450°C. Simultaneously, CuO and CuSO_4 act as catalysts for the selective catalytic reduction (SCR) of NO_x by ammonia to nitrogen and water. Regeneration is carried out with a reducing agent such as hydrogen, carbon monoxide or methane, which reduces CuSO_4 to metallic copper. The regeneration can take place at the same temperature as the SO_x/NO_x removal avoiding additional heating and cooling of the sorbent/catalyst. The regenerator off-gas is rich in SO_2 and can be further processed to sulphuric acid or elemental sulphur. After regeneration, the sorbent/catalyst can be oxidised and used for SO_x/NO_x removal again.

The main differences between the CuO processes proposed are related to the absorber design. We are studying a CuO process in which a relatively new contactor is applied, viz. the gas-solid trickle flow reactor [7,8]. In this reactor a dilute flow of sorbent/catalyst particles is contacted counter-currently with flue gas over a regularly stacked, inert packing. The reactor enables continuous operation, while the packing induces (i) a low pressure drop, (ii) limited axial dispersion in the gas and particle phase, and (iii) excellent heat and mass transfer between both phases.

Application in a continuous process with a gas-solid trickle flow absorber requires a special design of the sorbent/catalyst (see ref. 9). Therefore, a separate research project has been carried out at the University of Utrecht (The Netherlands), which has yielded several suitable sorbents/catalysts. They consist of a spherical silica support, prepared by Shell according to a sol-gel technique [11], with CuO deposited on this support through an ion-exchange technique [12,13]. The sulphation and regeneration kinetics of these silica-supported CuO sorbent/catalysts have been described in part I [9].

In this article, experimental results concerning the activity and selectivity of one of the sorbents/catalyst (hereafter "catalysts") for the catalytic reduction of NO_x by ammonia are discussed and compared with literature data. Special attention is paid to the influence of the fractional conversion from CuO to CuSO_4 , i.e. the sulphation degree.

The study focuses on the reduction of nitric oxide, which is the major component (90–95%) of most flue-gas NO_x . NO_x components not taken into account are nitrogen dioxide (5–10%) and nitrous oxide. Just like nitric oxide,

nitrogen dioxide contributes to the acid rain problem. Nitrous oxide is a relatively strong absorber of infrared radiation in the troposphere, and therefore it is likely to contribute to the greenhouse effect. Being stable in the troposphere, nitrous oxide is transported to the stratosphere, where it contributes to the depletion of ozone. Nitrous oxide production from oil and coal-fired boilers was first believed to occur up to a level of 25–40% of the NO_x total in the flue gas. Recent findings [14,15] reveal, however, that these high percentages are due to an artifact in the use of grab sampling techniques, and that in case of conventional boilers nitrous oxide is not a substantial fraction of flue-gas NO_x .

LITERATURE

Reactions

Although several CuO processes for the simultaneous removal of SO_x and NO_x have been developed up to demonstration-plant scale, the reduction of NO_x by ammonia catalysed by supported CuO or CuSO_4 received little attention in open literature. Yet, the behaviour of special SCR catalysts, such as alumina- or titania-supported V_2O_5 , Cr_2O_3 and Fe_2O_3 , was studied by many investigators. According to an extensive review of these studies by Bosch and Janssen [16], the following reactions may occur:

Up to a certain temperature, which depends on the type of catalyst, reduction reaction (1) generally predominates for dilute gas conditions, viz. for flue gas. Oxygen being involved in the reaction [reactions (3) and (4) occurring only to a small extent] and the formation of only small amounts of nitrous oxides have been reported many times. Inomata et al. [17], for instance, found for dilute gas conditions that the addition of oxygen considerably enhanced the nitric oxide–ammonia reaction on unsupported V_2O_5 catalysts. The production rate of nitrogen increased almost linearly with the oxygen concentra-

tion up to 1 vol -% O_2 , at higher concentrations, however, they observed only a slight increase. The production of nitrous oxide was low and independent of the oxygen concentration. Wong and Nobe [18] confirmed the substantial enhancement of the nitric oxide conversion by the presence of excess oxygen as well as the relatively small amounts of nitrous oxide formed for (mixtures of) V_2O_5 , Cr_2O_3 and Fe_2O_3 on Al_2O_3 and TiO_2 supports

At high temperatures and in the presence of oxygen, ammonia can be oxidised according to reactions (5–7). Obviously, this should be avoided, because it increases the consumption of ammonia, and it produces acidic compounds instead of removing them. Selectivity can thus be regarded as the relative contribution of reaction (1). High selectivity will lead to equal amounts of nitric oxide and ammonia converted with a high production level of nitrogen and a low production level of nitrous oxide.

In the case of a supported CuO or $CuSO_4$ catalyst, the same reactions seem to occur. Fukuzawa and Ishihara [19] investigated, amongst other catalysts, CuO supported on a bauxite support (approximately 79% Al_2O_3 , 8% SiO_2 , 10% Fe_2O_3 , 3% TiO_2) and prepared by impregnation. Experiments were carried out in fixed-bed reactors using either a controlled gas mixture (220–260 ppm NO, 300–350 ppm NH_3 , 0–4% O_2 , 12–14% CO_2 , 10–11% of water vapour and 0 or 1100 ppm SO_2) or actual flue gas. The presence of SO_2 in the gas caused a (slow) conversion of CuO to $CuSO_4$. For both the oxidised (CuO) and the sulphated ($CuSO_4$) catalyst they found a maximum level for the nitric oxide removal efficiency at a certain temperature. At higher temperatures, a large decrease in nitric oxide removal efficiency was observed due to the oxidation of ammonia by oxygen. The optimum temperature T_{opt} at which the maximum removal efficiency occurred was about 50°C higher for $CuSO_4$ than for CuO (350 and 300°C respectively). For temperatures $T < T_{opt}$, oxygen appeared to have an enhancing effect. The nitric oxide removal efficiency showed a strong increase up to 0.5% O_2 , but remained virtually constant for higher values of O_2 concentration. The enhancing effect of oxygen was also found by Nuyama et al. [20] for two catalysts consisting of an active carbon support impregnated with 0.64 and 6.0 wt -% $CuSO_4$, respectively. Furthermore, in the temperature range of 100 to 300°C formation of nitrous oxide hardly occurred, indicating the dominance of reduction reaction (1).

The different optimum temperatures for CuO and $CuSO_4$ found by Fukuzawa and Ishihara [19] may explain why several papers on CuO processes for the simultaneous removal of SO_x and NO_x report $CuSO_4$ to be a more effective catalyst for NO_x removal than CuO [6,21]. In the optimum temperature range for SO_x removal, which is 350–400°C, the nitric oxide removal efficiencies for $CuSO_4$ are considerably higher. Stelman et al. [5] tested impregnated CuO-on-alumina in a quartz fixed-bed reactor fed with simulated flue gas containing 500 ppm NO, 14.1% CO_2 , 3.5% O_2 and balance N_2 (no water vapour). At 400°C, a net nitric oxide production occurred for CuO caused by oxidation of ammonia.

to nitric oxide After the complete conversion of CuO to CuSO₄, however, 80–98% NO removal was obtained.

Reaction mechanisms and kinetics

Since vanadium oxide is one of the best catalysts for SCR (due to its high activity at relatively low temperatures ($T < 400^{\circ}\text{C}$) and its high resistance to poisoning by sulphur oxides), the reaction mechanisms and kinetics of SCR applying vanadium oxide catalysts were studied in detail by many investigators The opinion prevails that under dilute gas conditions and in the presence of oxygen, the dominating overall reaction (1) proceeds according to an Eley-Rideal type of mechanism [16,18,22,23]. Gaseous nitric oxide reacts with adsorbed ammonia, while oxygen is used to reoxidise the catalyst surface The reduction rate can then be expressed by the following equation

$$r = k_r KC_{\text{NH}_3} C_{\text{NO}} / (1 + KC_{\text{NH}_3}) \quad (8)$$

where:

$$k_r = k_0 \exp(-E_a/RT) \quad (9)$$

K represents the equilibrium constant of the adsorption isotherm for ammonia In terms of overall reaction orders, this means that an order between 0 and 1 may be found for ammonia depending both on the value of the equilibrium constant K and on the experimental concentration range for ammonia At a given equilibrium constant K , the ammonia concentration will become involved in the reduction rate below a certain concentration level Wong and Nobe [18], among others, determined a zero order in ammonia (and a first order in nitric oxide) for 10 wt.-% V₂O₅ on Al₂O₃ or TiO₂ catalysts at temperatures up to 350°C In their experiments, the nitric oxide and ammonia concentrations were varied between 200 and 2000 ppm, while the oxygen concentration was kept constant at 2.2 vol.-%. They also carried out experiments for catalysts containing 10 wt.-% Cr₂O₃, Fe₂O₃ or mixtures of these metal oxides and V₂O₅ on an Al₂O₃ or TiO₂ support, and found the same reaction orders The activation energies ranged from about 40 to 60 kJ/mol, which is in agreement with data reported by many other investigators [16] The similarities in the reaction of kinetics of these different catalysts suggest that the reaction mechanism at low temperatures (i.e., below the temperature of maximum nitric oxide conversion) is essentially the same

In contradiction with the prevailing opinion presented above, several authors have reported reaction orders between 0 and 1 in both nitric oxide and ammonia [16] This indicates that the intrinsic reaction rate was determined by the reaction of adsorbed nitric oxide with adsorbed ammonia. In that case, a Langmuir-Hinshelwood type rate expression would provide a better description of the kinetic behaviour

TABLE 1

Properties of the np (5 7) catalyst investigated, and of catalysts studied by Wong and Noble ([18], V_2O_5 - TiO_2 and V_2O_5 - Al_2O_3) and by Fukuzawa and Ishihara ([19], $CuO/CuSO_4$ -bauxite and $CuO/CuSO_4-Al_2O_3$)

Catalyst	$CuO/CuSO_4-SiO_2$ (np (5 7))		$V_2O_5-TiO_2$	$V_2O_5-Al_2O_3$	$CuO/CuSO_4$ -bauxite	$CuO/CuSO_4-Al_2O_3$
Support	SiO_2 Shell-S980Al 5		TiO_2	Al_2O_3 Filtrol gr 86	bauxite ^a moulded	Al_2O_3
Particle dia (mm)	1.5		3.2×3.2 pellets	3.2×3.2 pellets	3.5×2.9 pellets	3.0
Mean pore dia (nm)	15		50	9.2	9.0	8.6
Pore volume (ml/g)	1.0		0.32	0.46	0.26	0.68
Surface area (m^2/g)	265		26	200	210	367
App density (kg/m^3)	750		1570	1080	-	-
Deposition technique	ion-exchange		impregn	impregn	impregn	impregn
Metal content (wt.-% of oxidised sorbent)	5.7		5.3	5.3	5	5

^aApproximate composition of the bauxite support 79% Al_2O_3 , 8% SiO_2 , 10% Fe_2O_3 , 3% TiO_2

Explicit kinetic data on the selective catalytic reduction of nitric oxide by ammonia over CuO or CuSO₄ catalysts under dilute gas conditions and in the presence of excess oxygen are very scarce. Fukuzawa and Ishihara [19] derived a first order dependence on the NO_x concentration and an activation energy of 42 kJ/mol for 1.00–1.19 mm diameter CuO/CuSO₄-on-bauxite particles. Nuyama et al. [20] reported the reaction orders in both nitric oxide and ammonia to depend on the reaction temperature for their 240–500 μm CuSO₄-on-active-carbon particles. From continuous flow experiments in a fixed-bed reactor, they derived the following orders in nitric oxide (n) and ammonia (m) at 100°C $n=1.1$ $m=0.1$, at 150°C $n=1.1$ $m=0.1$, at 200°C $n=0.6$ $m=0.2$ and at 250°C $n=0.6$ $m=0.3$. Several other studies [6,21] on SCR with CuO/CuSO₄ catalysts predominantly deal with the influence of the NO_x concentration and the NO_x/NH₃ molar ratio at the reactor inlet on the overall reactor performance, and do not provide enough information on e.g. gas–solids mass transfer and pore diffusion rates to enable conclusions about intrinsic kinetics and reaction mechanisms.

EXPERIMENTAL

Catalyst properties

The silica-supported CuO catalyst investigated was developed at the University of Utrecht, The Netherlands [10,12]. The support of the catalyst consists of porous silica spheres (1.5 mm average diameter) with a high mechanical strength and a narrow pore size distribution, which are manufactured by Shell according to a sol-gel technique [11]. Physical properties of the support are given in Table 1. An ion-exchange technique was applied to create a uniform, highly dispersed CuO deposition [9,12]. The silica spheres were suspended in a continuously stirred, aqueous solution of Cu(NO₃)₂, which was brought to pH 10 by adding concentrated ammonia. According to Kohler et al. [13], under these conditions [Cu(NH₃)₄]²⁺-ions are exchanged with the hydroxyl protons present on the initial silica surface or generated during the exchange at elevated pH, until equilibrium is reached. Subsequently, the loaded silica spheres were dried and calcined at 450°C. The catalyst particles tested in this study were obtained from a 5 kg batch, prepared for bench-scale testing by Engelhard Co. (The Netherlands). The catalyst is coded np(5.7), where np stands for “narrow pore” referring to its relatively small average pore diameter, and with the copper content determined by chemical analysis given in parentheses.

Apparatus and experimental methods

The catalytic activity of the np(5.7) catalyst was tested in a fixed-bed microreactor (inner diameter 10 mm), made of quartz and placed in a tubular

Fig 1 Flow diagram of the experimental set-up 1 Microreactor, 2 sample for nitrous oxide analysis, 3 bubbler (HCl solution), 4 cold trap (melting ice), 5 gas saturator

oven (see Fig 1) The 1.5 mm diameter catalyst particles were ground and sieved, and the diameter fraction of 100–150 μm was used for the fixed-bed experiments. Most of the experiments were carried out with 375 mg catalyst particles resulting in a bed height of 10.5 mm and a bed porosity of 0.44.

Before the start of an experiment, the catalyst particles were pretreated in the following way:

- 1 Calcination in nitrogen at 450°C
- 2 Reduction of CuO to Cu using a gas mixture of 18% H_2 , 10% H_2O and balance N_2 at 375°C
- 3 Oxidation of Cu to CuO using a gas mixture of 5% O_2 , 10% H_2O and balance N_2 at 375°C
- 4 Partial sulphation by leading a gas mixture of 1000 ppm SO_2 , 5 vol.-% O_2 and 10 vol.-% H_2O in N_2 through the catalyst bed at 375°C.

Steps 1–3 are identical to the pretreatment procedure applied in the thermogravimetric measurements, which were carried out to determine the sulphation

and regeneration kinetics. As described in part I [9], the resulting sorbent/catalyst showed a constant SO_2 absorption activity in up to 75 subsequent cycles of sulphation and regeneration.

The partial sulphation (step 4) was controlled by leading the gas mixture through the bed during a certain time interval. Controlled partial sulphation enabled an accurate determination of the influence of the sulphation degree on the SCR performance of the catalyst. Calculation of the time needed to reach the desired sulphation degree was based on the following assumptions

— The SO_2 concentration in the catalyst bed is constant throughout the bed volume

— The reaction kinetics are rate determining

— The catalyst bed is isothermal

With these assumptions, the fractional conversion x_s should be equal throughout the bed and the sulphation time needed to reach a certain value of x_s can be calculated from the intrinsic reaction rate expression derived earlier from thermo-gravimetric measurements (see part I, [9]) as:

$$r = \frac{\zeta \rho_s}{M_{\text{Cu}}} \frac{dx_s}{dt} = k_r C_{\text{SO}_2} (1 - x_s) \quad (10)$$

In eqn. (10), ζ represents the copper weight fraction of the oxidised catalyst ($\zeta = 0.057$), ρ_s is the apparent density of the catalyst particles ($\rho_s = 750 \text{ kg/m}^3$) and M_{Cu} is the molecular mass of metallic copper ($M_{\text{Cu}} = 63.5 \cdot 10^{-3} \text{ kg/mol}$). According to the experimental results described in part I [9], the intrinsic reaction rate constant for sulphation k_r can be expressed as: $k_r = 6.6 \cdot 10^7 \exp(-86 \cdot 10^3/RT)$. Integration of eqn (10) yields

$$t = -\frac{\zeta \rho_s}{M_{\text{Cu}} k_r C_{\text{SO}_2}} \ln(1 - x_s) \quad (11)$$

In fact, both the fractional conversion and the SO_2 concentration are a function of the axial position in the packed bed due to the absorption of SO_2 . However, eqn (11) can be used for a close estimation of the sulphation time needed for a certain average sulphation degree, if only a limited percentage of the SO_2 in the gas phase is absorbed in the bed (differential reactor). This applies for the chosen experimental conditions. The maximum decrease in the SO_2 concentration over the packed bed, occurring for $x_s = 0$, was limited to approximately 30% assuming plug flow for the gas phase [$C(\text{out})/C(\text{in}) = 0.70$]

To account for a decreasing SO_2 concentration over the bed, an average SO_2 concentration was used in eqn (11), defined as

$$(C_{\text{SO}_2})_{\text{av}} = \frac{C(\text{in}) + \frac{C(\text{out})_{x_s=0} + C(\text{out})_{x_s=x_s^*}}{2}}{2} \quad (12)$$

with x_s^* being the required value of the fractional conversion x_s . The sulphation times, calculated according to eqns (11) and (12), and applied to achieve the sulphation degrees investigated, are given in Table 2

After the catalyst particles were pretreated, they were contacted with a standard gas mixture consisting of 1000 ppm NO, 1000 ppm NH₃, 3 vol -% O₂ and 10 vol -% H₂O in N₂ to test their SCR performance. The flow-rates of 5% NO/N₂, 5% NH₃/N₂, O₂ and N₂ were adjusted by mass flow controllers. Water vapour was added to the gas mixture by means of a blubber, which was placed in a thermostated bath. In this blubber complete saturation was achieved. The water vapour concentration could therefore be controlled by setting the temperature of the thermostated bath. All the gas supply tubing behind the thermostated bath was kept at a temperature of about 80°C to prevent condensation of the water vapour. The total gas flow-rate to the fixed bed amounted to 300 ml/min at 0°C and 1 atm (space velocity 21 800 h⁻¹).

Concentrations of nitrogen containing components present in the outlet gas stream were measured by applying three different techniques. First, the NO/NO₂ concentrations in the outlet gas stream were determined on-line using a chemiluminescent analyzer (Beckman 951A, 0–10000 ppm). Before entering the analyzer, the outlet gas stream was passed through a cold trap and subsequently dried to remove ammonia and water vapour. Secondly, a wet chemical method was used to measure the ammonia concentration. For this method, the outlet gas stream was led through a 100 mol/m³ hydrochloric acid solution for a fixed time interval, and the ammonia accumulated in this solution as ammonium ions. Subsequent addition of an alkaline solution of potassium mercury iodide (Nessler's reagent), which resulted in a brownish solution, enabled a spectrophotometric determination of the ammonium concentration. Finally, the nitrous oxide (N₂O) concentration was determined using a grab sampling technique and off-line gas chromatography. Gas samples were withdrawn just behind the reactor outlet and collected in a 1000 ml pyrex container. Subsequently, the samples were analysed in a gas chromatograph equipped with a Chromosorb 102/10% THEED separation column and a thermal conductivity

TABLE 2

Sulphation times, calculated according to eqns (11) and (12), and applied to achieve the desired sulphation degrees

Sulphation degree x_s (-)	Sulphation time t (s)
0.05	275
0.30	1875
0.80	4100 ^a

^aInlet SO₂ concentration 2000 ppm instead of 1000 ppm

detector The above-mentioned artifact in the use of grab sampling techniques, viz a considerable production of nitrous oxide in the container causing an overestimation of the nitrous oxide concentration, did not occur here because the gas mixture did not contain any SO_2 . Muzio et al [15] clearly demonstrated that the presence of SO_2 in the gas mixture is a prerequisite for the formation of nitrous oxide in a pyrex container

From tests with different particle sizes and gas flow-rates respectively, it was established that the experimental reaction rates were never limited by pore diffusion or external mass transfer. Furthermore, during the experiments no temperature rise of the catalyst bed could be detected

RESULTS AND DISCUSSION

Selectivity

First, the selectivity of the catalyst towards the reduction of nitric oxide by ammonia according to reaction (1) was investigated as a function of the bed temperature for sulphation degrees of 0 and 80%. The resulting outlet concentrations for nitric oxide, ammonia and nitrous oxide are shown in Fig 2 (0% sulphation) and Fig. 3 (80% sulphation) For both sulphation degrees the conversions of nitric oxide and ammonia over the catalyst bed increase almost equally with increasing temperature, up to a certain temperature level (approximately 325°C and 375°C in case of 0% and 80% sulphation respectively) At the same time, only a very small amount of nitrous oxide is produced. This implies a predominance of reduction reaction (1), i.e. the selective catalytic

Fig 2 Nitric oxide (+), ammonia (□) and nitrous oxide (○) concentrations at the fixed-bed gas outlet as a function of the bed temperature for fresh np(57) catalyst particles containing CuO only

Fig 3 Nitric oxide (+), ammonia (□) and nitrous oxide (○) concentrations at the fixed-bed gas outlet as a function of the bed temperature for np(5 7) catalyst particles with a sulphation degree of 80%

reduction of nitric oxide At higher temperatures, the nitric oxide outlet concentrations pass through a minimum and subsequently increase again. This is accompanied by a strong decrease of the outlet ammonia concentration and an increase of the nitrous oxide production. Apparently, oxidation of ammonia according to reactions (5–7) starts to occur, causing a decreasing selectivity of the catalyst towards reaction (1). This observation is in agreement with literature data on various other catalysts.

The temperature at which the minimum nitric oxide outlet concentration (i.e. the maximum nitric oxide removal efficiency) appears is about 70°C higher for the catalyst with 80% sulphation than for the catalyst with CuO only (420 and 350°C respectively). In addition, this minimum value of the nitric oxide outlet concentration is clearly lower for the catalyst with a sulphation degree of 80% (350 ppm versus 500 ppm for the catalyst with CuO only). Consequently, the nitric oxide removal efficiencies are considerably higher for the sulphated catalyst in the optimum temperature range (350–400°C) for SO_x removal. In other words, the CuSO₄ form is more effective for NO_x removal in case of simultaneous SO_x removal than the CuO form, which is in agreement with literature data reported for γ-alumina supported CuO/CuSO₄ catalysts [5,6,21].

Influence of the sulphation degree on the SCR performance of the catalyst

Fig 4 shows the nitric oxide outlet concentration as a function of the bed temperature for different sulphation degrees x_s . It appears that, for temperatures below 350°C, there are in fact only two curves, viz. one for fresh catalyst

Fig 4 Nitric oxide concentration at the fixed-bed gas outlet as a function of the bed temperature for np(5.7) catalyst particles with different sulphation degrees x_s and for regenerated np(5.7) catalyst particles (which were previously sulphated up to $x_s = 0.80$)

particles with CuO only and a single one for catalyst particles containing various different fractions of CuSO_4 as a result of controlled partial sulphation (the effect of regeneration will be discussed later). Obviously, catalyst particles with a sulphation degree of only 5% yield the same nitric oxide removal efficiency as catalyst particles with a sulphation degree of 80%. At temperatures above 350°C, however, different sulphation degrees cause a different behaviour. At increasing x_s , the minimum nitric oxide outlet concentration becomes lower while occurring at a higher temperature level. Apparently, the selectivity of the catalyst towards the reduction of nitric oxide according to reaction (1) persists up to a higher temperature for increasing sulphation degrees. Finally, it should be noticed that the temperature for which the nitric oxide outlet concentration is minimal, does *not* increase *linearly* with increasing x_s , a conversion of only 5% has a relatively large effect.

After regeneration of catalyst particles with a sulphation degree of 80%, i.e. reduction by hydrogen followed by re-oxidation, the catalytic behaviour of the catalyst shown in Fig 4 (closed symbols) is close to that of fresh catalyst particles with a sulphation degree of 5%. This is probably due to the formation of some Cu_2S during the reduction of CuSO_4 , which is oxidised to CuSO_4 again in the subsequent oxidation step. The formation of Cu_2S and its subsequent oxidation to CuSO_4 have been reported in literature for several other supported CuO sorbents/catalysts [2,4]. Furthermore, this explanation is in agreement with findings reported in part I [9]. There it has been estimated from sulphation/regeneration cycles with the np(5.7) sorbent/catalyst in a microbalance set-up that, after regeneration, 3.5–8.5% of the copper is present as CuSO_4 . The formation of Cu_2S increases the consumption of reducing agent and it

decreases the capacity of the sorbent/catalyst for SO_x removal. However, if the behaviour of the regenerated catalyst, shown in Fig. 4, is explained by Cu_2S formation, it clearly has a beneficial effect on the overall NO_x removal efficiency in case of simultaneous removal of SO_x and NO_x at 350–400°C.

Influence of water vapour

To get an impression of the influence of water vapour on the SCR activity of the catalyst, a separate experiment was carried out without water vapour in the gas mixture and using fresh catalyst particles containing CuO only. From the nitric oxide outlet concentration versus bed temperature curves presented in Fig. 5 it appears that water vapour reduces the catalytic activity of the fresh CuO catalyst for the reduction reaction (1) as well as for the oxidation of ammonia (reactions 5–7). In case of a gas mixture containing 10% water vapour, the temperature at which the minimum nitric oxide outlet concentration appears is approximately 50°C higher than in the absence of water vapour ($T_{\text{opt}} = 350^\circ\text{C}$ and 300°C respectively). Consequently, the presence of 10% water vapour has a large positive effect on the NO_x removal efficiency in the optimum temperature range for simultaneous SO_x and NO_x removal (350–400°C).

Reaction kinetics

The study of the reaction kinetics was limited to those temperatures, at which only the selective catalytic reduction of nitric oxide by ammonia according to

Fig. 5 Effect of the presence of water vapour in the gas mixture on the nitric oxide conversion over the fixed bed as a function of the bed temperature for fresh np(5.7) catalyst particles containing CuO only

reaction (1) occurred. From experiments with an inlet concentration of 500 instead of 1000 ppm for nitric oxide and ammonia, respectively, the reaction rate was estimated to be first order in nitric oxide and zero order in ammonia. These orders were assumed to be valid for all experimental concentrations, although the experimental results do not preclude the possibility of an Eley-Rideal type of rate expression with an overall order in ammonia increasing from zero to one over the ammonia concentration range from 250 to 0 ppm.

With orders of one and zero for nitric oxide and ammonia, respectively, the intrinsic reduction rate can be expressed as:

$$r = k_r C_{\text{NO}} \quad (13)$$

Then, assuming (i) plug flow for the gas phase and (ii) the reaction kinetics to be rate limiting, the intrinsic reaction rate constant k_r can be calculated from the nitric oxide inlet and outlet concentrations according to

$$k_r = -\frac{U_g}{(1-\epsilon)L} \ln [C_{\text{NO}}(\text{out})/C_{\text{NO}}(\text{in})] \quad (14)$$

Fig. 6 shows Arrhenius plots of k_r versus the bed temperature T for various sulphation degrees of the fresh catalyst as well as the regenerated catalyst, from which the activation energy E_a and the frequency factor k_0 were derived. The following expression was found for the intrinsic reaction rate constant of the fresh catalyst containing CuO only ($T \leq 330^\circ\text{C}$)

$$k_r = 9.2 \cdot 10^6 \exp(-68 \cdot 10^3/RT) \quad (15)$$

Fig. 6 Arrhenius plot of the intrinsic reaction rate constant k_r versus bed temperature for np(5.7) catalyst samples with various different sulphation degrees and for regenerated np(5.7) catalyst (which was previously sulphated up to $x_s = 0.80$)

For the fresh catalyst being partially sulphated to sulphation degrees of 5, 30 or 80%, and for the regenerated catalyst, k_r was derived to be ($T \leq 375^\circ\text{C}$)

$$k_r = 1.6 \cdot 10^7 \exp(-73 \cdot 10^3/RT) \quad (16)$$

Both activation energies are considerably higher than the value of 42 kJ/mol reported by Fukuzawa and Ishihara [19] for 1.00–1.19 mm diameter crushed CuO/CuSO_4 -on-bauxite particles, but only little higher than reported by several other investigators for V_2O_5 -containing catalysts. Possibly, the data presented by Fukuzawa and Ishihara were influenced to some extent by pore diffusion.

In Fig 7, the experimentally determined catalytic activity of the partially sulphated np(5.7) catalyst towards the reduction of nitric oxide with ammonia is compared with literature data. The experimental data for fresh np(5.7) cat-

Fig 7 Comparison of experimental values of the intrinsic reaction rate constant k_r for the np(5.7) catalyst with literature data given by Wong and Nobe [18] for 10 wt-% V_2O_5 on TiO_2 or Al_2O_3 catalysts, and with data given by Fukuzawa and Ishihara [19] for CuO/CuSO_4 on bauxite or Al_2O_3 catalysts. Catalyst properties are listed in Table 1. Also shown are modified reaction rate constants for sulphation of the reduced and the oxidized catalyst, according to eqns (17) and (18) respectively, with the sulphation degree x_s ranging from 0 to 0.50.

alyst containing CuO only are not presented here, because they are of little importance when the catalyst is applied in a process for simultaneous removal of SO_x and NO_x from flue gases. In that case, they only represent the behaviour of the catalyst at the start of its first sulphation/regeneration cycle. The upper temperature limit of the literature data corresponds to the temperature at which direct oxidation of ammonia by oxygen starts to occur.

Fig 7 clearly shows that the activity of the np(5 7) catalyst is low compared with the activity of the V₂O₅-containing catalysts, for which a TiO₂ support is generally found to yield a higher catalytic activity than an Al₂O₃ support [16]. When compared to data of Fukuzawa and Ishihara [19] for CuO/CuSO₄ on Al₂O₃ or bauxite, however, the reaction rate constant is of the same order of magnitude, but the catalytic activity occurs at a (somewhat) higher temperature level. This is in agreement with findings of Nishijima et al [24], who studied the catalytic activity of CuBr₂ on a γ-Al₂O₃ and on a SiO₂ support.

Since the catalyst is to be applied in a process for the simultaneous removal of SO_x and NO_x, the temperature range with a high SCR activity should preferably coincide with the proper temperature range for SO_x removal. To show whether this is the case, the sulphation rate constants for the investigated np(5 7) catalyst (including the influence of the sulphation degree and the oxygen concentration on the reaction rate) are presented in Fig. 7 as well. As described in detail in part I [9], two different expressions for the sulphation rate can be derived depending on whether or not the sorbent/catalyst undergoes a separate pre-oxidation between reduction and SO_x absorption. In both cases, the sulphation rate is first order in the SO₂ concentration. The modified rate constants shown in Fig. 7 were found to be expressed by eqns (17) and (18) for sulphation of the oxidised and the reduced sorbent/catalyst respectively:

$$k_r = 6.6 \cdot 10^7 \exp(-86 \cdot 10^3/RT) (1 - x_s) \quad (17)$$

$$k_r = 4.0 \cdot 10^8 \exp(-86 \cdot 10^3/RT) C_{O_2}^{0.15} (1 - 1.5x_s) \quad \text{for } x_s \leq 0.50 \quad (18)$$

Without separate pre-oxidation, sulphation and oxidation will occur simultaneously, which was found to have a large beneficial effect on the sulphation rate up to a sulphation degree of approximately 50%. Beyond this sulphation degree, the sulphation rate in case of simultaneous oxidation and sulphation rapidly decreased to values even lower than in case of separate pre-oxidation. For the thermogravimetric measurements described in part I [9] this was attributed to (i) a temperature increase of the copper deposits due to the exothermic oxidation and (ii) structural effects as a result of the simultaneous occurrence of both reactions. In a previous article [8], reporting on experiments in a bench-scale plant of the entire CuO process (gas-solid trickle flow absorber, regenerator and continuous sorbent/catalyst transport between them), it was shown that the beneficial effect of simultaneous oxidation and sulpha-

tion also occurs in the gas-solid trickle flow absorber. Consequently, direct introduction of reduced sorbent/catalyst into the gas-solid trickle flow absorber is the most favourable operating mode yielding higher rates of sulphation. The values of the rate constant for SCR of nitric oxide with ammonia should therefore be compared with values of the modified rate constant for sulphation of reduced sorbent/catalyst to judge the feasibility of the simultaneous removal of SO_x and NO_x with this sorbent/catalyst.

It appears that up to approximately 375°C ammonia reacts selectively with nitric oxide, and the reaction rate constants for SCR of nitric oxide and for direct sulphation of reduced sorbent/catalyst are of the same order of magnitude. This indicates that the simultaneous removal of SO_x and NO_x is possible up to this temperature. At higher temperatures, the sorbent/catalyst shows a further increase of the sulphation rates (up to approximately 450°C , where CuSO_4 formed starts to dissociate), but at the same time a loss of selectivity towards the reduction of nitric oxide by ammonia occurs. An increase of the temperature up to which the selectivity holds by suppressing the direct oxidation of ammonia by oxygen (further sorbent/catalyst development) would therefore lead to a more efficient removal of SO_x and NO_x . It should be noted, however, that operating the absorber at a temperature level beyond $350\text{--}375^\circ\text{C}$ will generally necessitate changes in boiler-design in order to increase the flue gas temperature at the economiser outlet.

CONCLUSIONS

The activity and selectivity with respect to catalytic reduction of nitric oxide by ammonia were determined as a function of temperature for a silica-supported CuO catalyst. Before the start of the nitric oxide reduction experiments, the catalyst particles were partially sulphated (to sulphation degrees of 0, 5, 30 or 80%) to investigate the influence of the sulphation degree on the SCR behaviour. The nitric oxide reduction experiments were carried out in a fixed-bed microreactor using a standard gas mixture consisting of 1000 ppm NO, 1000 ppm NH_3 , 3% O_2 and 10% H_2O in N_2 . From the experimental results the following conclusions can be drawn:

- Up to a certain optimum temperature, all catalyst samples investigated show a high selectivity towards the reaction of NO with NH_3 and O_2 to N_2 and H_2O , irrespective of their degree of sulphation. At higher temperatures, simultaneous oxidation of NH_3 by O_2 starts to occur causing a decrease of the NO removal efficiency.

- The optimum temperature at which the maximum NO removal efficiency is reached is approximately 350°C for the fresh catalyst containing CuO only. At an increasing sulphation degree, this optimum temperature increases up to 420°C for a sulphation degree of 80%. The maximum NO removal efficiency increases as well. Consequently, in the optimum temperature range for SO_x

removal (350–400°C) the effectivity for NO reduction increases with an increasing sulphation degree of the catalyst

— Limited conversion of CuO to CuSO₄ has a relatively large effect on the catalytic behaviour of the catalyst

— After regeneration of catalyst particles with a sulphation degree of 80%, i.e. reduction by hydrogen followed by re-oxidation, the catalytic behaviour is similar to that of fresh catalyst particles with a sulphation degree of 5%. This is attributed to the formation of some Cu₂S during the reduction, which is oxidised to CuSO₄ in the subsequent oxidation step.

— For the fresh catalyst containing CuO only, the presence of 10% water vapour in the gas mixture reduces the catalytic activity regarding the reaction of NO with NH₃ and O₂ to N₂ and H₂O, but it also reduces the catalytic activity for the oxidation of NH₃ by O₂.

— For NO and NH₃ concentrations of 250–1000 ppm, the reaction rate of the selective catalytic reduction of NO by NH₃ is first order in NO and zero order in NH₃ for all the states of the catalyst investigated.

— The catalytic activity of the partially sulphated silica-supported CuO catalyst is up to 100 times lower than the activity of supported V₂O₅ catalysts, which have been developed especially for selective catalytic reduction of NO by NH₃. However, the selectivity of the partially sulphated silica-supported CuO catalyst towards this catalytic reduction is maintained up to a temperature of about 375°C, which enables application of the (sorbent/)catalyst in a process for simultaneous removal of SO_x and NO_x. The reaction rate constants for SO_x and NO_x removal appeared to be of the same order of magnitude provided that the reduced (sorbent/)catalyst enters the absorber directly, i.e. without a separate pre-oxidation

NOTATION

C	concentration of gaseous reactant	$\text{mol (m}_g\text{)}^{-3}$
E_a	activation energy	J mol^{-1}
k_0	frequency factor of the intrinsic reaction rate constant (first order reaction)	$(\text{m}_g)^3 (\text{m}_{\text{cat}})^{-3} \text{s}^{-1}$
k_r	intrinsic reaction rate constant (first order reaction)	$(\text{m}_g)^3 (\text{m}_{\text{cat}})^{-3} \text{s}^{-1}$
K	equilibrium constant	$\text{m}^3 \text{mol}^{-1}$
L	bed height	m
M	molar mass	kg mol^{-1}
r	intrinsic reaction rate	$\text{mol (m}_{\text{cat}}\text{)}^{-3} \text{s}^{-1}$
R	gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
t	time	s
T	temperature	K
U_g	superficial gas velocity	m s^{-1}

x_s fractional conversion of CuO to CuSO₄, or sulphation degree

Greek symbols

ϵ void fraction of the catalyst bed

ζ Cu weight fraction of oxidised catalyst

ρ_s apparent density of oxidised catalyst kg m^{-3}

Subscripts

cat catalyst

g gas phase

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